

AD722092

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DEVELOPMENT OF CHALCOPYRITE CRYSTALS FOR  
NONLINEAR OPTICAL APPLICATIONS

Interim Technical Report No. 1

for

Contract F33615-70-C-1640

for the period

1 August - 31 October 1970

M. L. Report No. 1896

October 1970

Sponsored by  
Advanced Research Projects Agency  
ARPA Order No. 1636

Prepared for  
Air Force Materials Laboratory  
Wright-Patterson Air Force Base, Ohio

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**Contractor:** The Board of Trustees of the Leland Stanford Jr. University

**Contract No.** F33615-70-C-1640

**ARPA Order Number** 1636

**Program Code Number** OD10

**Effective Date of Contract:** 1 August 1970

**Contract Expiration Date :** 31 July 1971

**Amount of Contract :** \$60,000

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## I. PURPOSE OF THIS WORK

Research is being conducted to grow and evaluate crystals of the chalcopyrite class for use in nonlinear optical applications, modulator applications and semiconductor applications. Toward this goal attempts to grow single crystals are being made with appropriate measurements and evaluation of each crystal sample obtained.

## II. PROGRESS THIS QUARTER

This report reviews progress in the growth of chalcopyrite crystals for both this quarter and for the year preceding the start of this work. The previous effort, sponsored by Center for Materials Research at Stanford University, led to the results reported here for this quarter and is included to provide continuity in the description of the research effort.

Effort to obtain a single crystal of  $\text{CdGeAs}_2$  began in October, 1969. This particular crystal was chosen because of its infrared transparency range from  $2\ \mu$  to  $30\ \mu$  and its relatively large tetragonality factor which could possibly lead to a large birefringence. The crystal had also been investigated in Russia and its index of refraction and relative nonlinear coefficient measured. These values are respectively,  $n \approx 3.6$  and  $\delta \approx \delta^{\text{GaAs}}/2$ . It was felt that an effort in crystal growth should be limited to a single material at a time. In this way maximum progress could be made so that evaluation of the crystal properties could be accomplished as quickly as possible.

The growth properties of interest included homogeneity, structural integrity, singularity, surface quality and stoichiometry. Arsenic concentration as part of crystal stoichiometry is especially important due to its high vapor pressure and rapid rate of diffusion in the material.

The semiconductor properties that are considered important include free carrier density, resistivity, mobility and impurity concentration. The optical properties of interest include transparency, free electron absorption, index of refraction and birefringence, nonlinear coefficients, electro-optical coefficients and photoelastic constants. Measurement of optical properties, for the most part, require the availability of a single crystal sample.

The initial crystal growth effort was spent learning to properly melt crystal elemental constituents to form a mixture. This problem was aggravated by the high vapor pressure of arsenic and the lack of strength of quartz vessels at elevated temperatures. For example, the vapor pressures and reaction temperatures for Cd , Ge and As are shown in Table I. Successive runs were taken with increasing temperature in order to find the temperature at which the components melted and mixed properly. It was found that in a flat temperature gradient at  $730^{\circ}\text{C}$  the material melted and appeared homogeneous.

Following the successful melting of the components an attempt was made to grow a single crystal by a modified Bridgeman technique. The melting point of  $\text{CdGeAs}_2$  is  $670^{\circ}\text{C}$  which was well within the capability of the growth oven. However, the crystal is sphalerite at temperatures above  $630^{\circ}\text{C}$  and chalcopyrite at temperatures lower than this. It was

TABLE I

Vapor Pressures of Arsenic and Cadmium

	Temperature °C				
	1 mm	10 mm	100 mm	1 atm	10 atm
Arsenic	327°C	437°C	518°C	610°C	~730°C
Cadmium	394°C	484°C	611°C	765°C	~970°C

TABLE II

#19 - CdGeAs<sub>2</sub> Growth Conditions

Source:	Zone refined CdGeAs <sub>2</sub>		
Purity:	6 nines		
Weights:	10.068 grams Cd, 6.498 grams Ge, 13.824 grams As (2% As excess)		
Crucible:	Quartz (Englehart) 13 mm × 5½" with 1½" × 1/8" capillary		
Gradient:	32°/cm		
Lowering Rate:	.015"/hr		
ΔT/hr:	1.2°/hr		
Cool Rate:	2.6°/hr		
Begin:	9-3-70 3:00		
Stop:	9-16-70 5:00		
Results:	Boule length 4"		
Etch:	Grain boundaries	H <sub>2</sub> O <sub>2</sub> :	NH <sub>4</sub> OH: H <sub>2</sub> O
	Visible	1 :	2 : 4

expected that some crystal cracking would occur as the material was cooled through this region. Cracking was observed on all single crystal growth attempts. Fortunately, large enough single crystal regions were obtained for some analysis to be made. The growth effort continued for 11 attempts during which time oven parameters and crystal composition were changed.

The growth conditions were generally as given in Table II. Figure 1 shows a photograph of boule #13 and Fig. 2 shows the oven gradient that was used during growth.

Analysis and measurements were performed on boules #13 to #19 for the arsenic content and distribution in the boule. Also, optical measurements were performed of polycrystalline samples large enough for transmission measurements to be made. The arsenic microanalysis record for the boules is shown in Fig. 3. Note that the arsenic concentration is high at the bottom or seed end of the boule and then decreases toward the boule center. The large increase of arsenic at the top end of the boule is expected since excess arsenic is driven that way by the growth process.

Optical transmission measurements were taken of the boule sections. None of the sections from the top end, excess arsenic present, were transparent. The middle of the boules were also nearly opaque. The bottom, or seed end, of the boules showed transparency from 2  $\mu$  to 18  $\mu$  with obvious free electron cutoff occurring at 18  $\mu$ . It is expected that improvements in the crystal transparency range toward the 30  $\mu$  limit will be made as the crystal arsenic content is controlled.

Following the growth of boule #19 and the identification of an arsenic stoichiometry problem, a zone refining apparatus was constructed. The equipment was built by CMR technicians starting in September, 1970. The

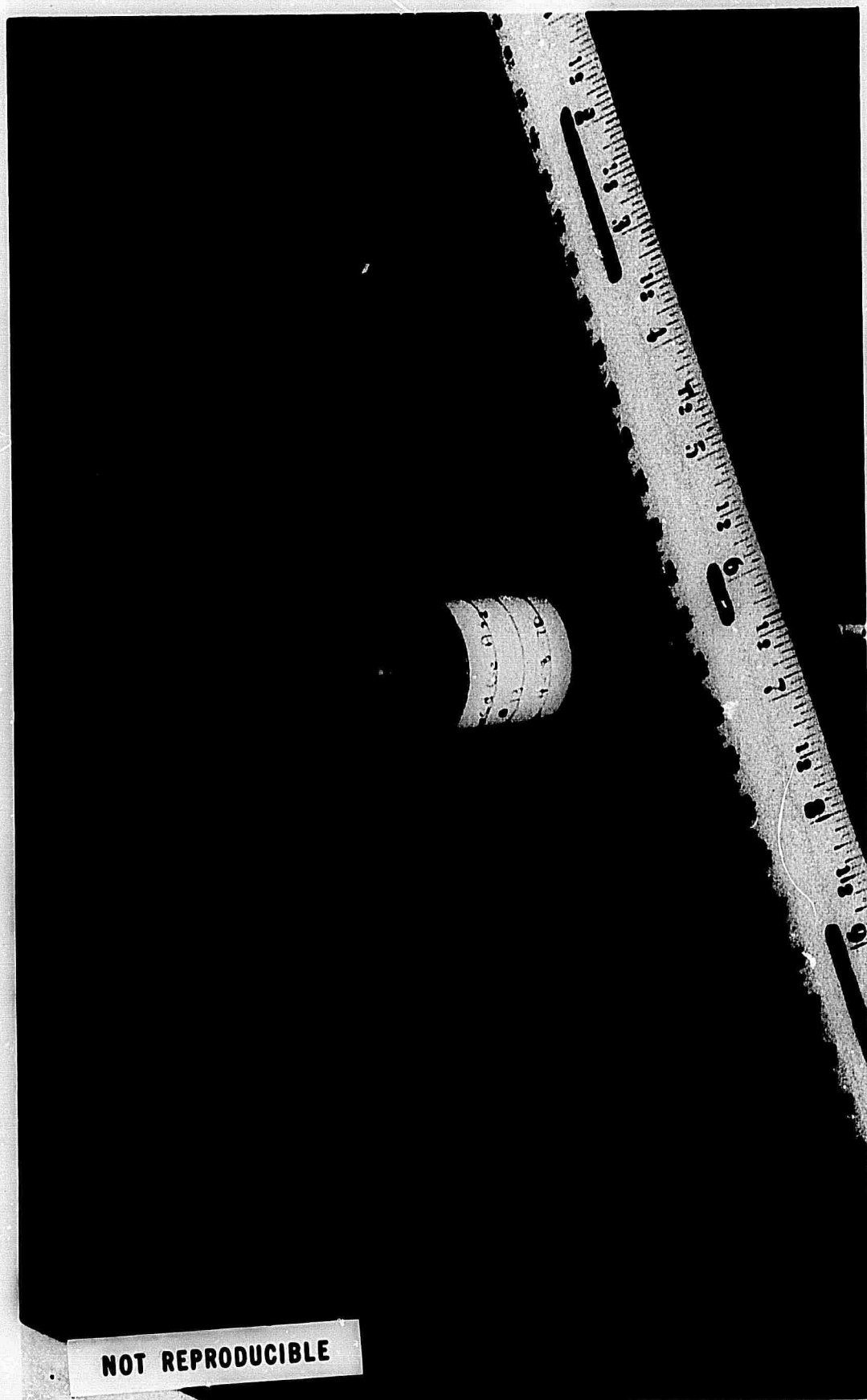


FIG. 1.--Photograph of boule No. 13 of GdGeAs<sub>2</sub>. The sample was polycrystalline with grain sizes up to 2 mm<sup>3</sup>.

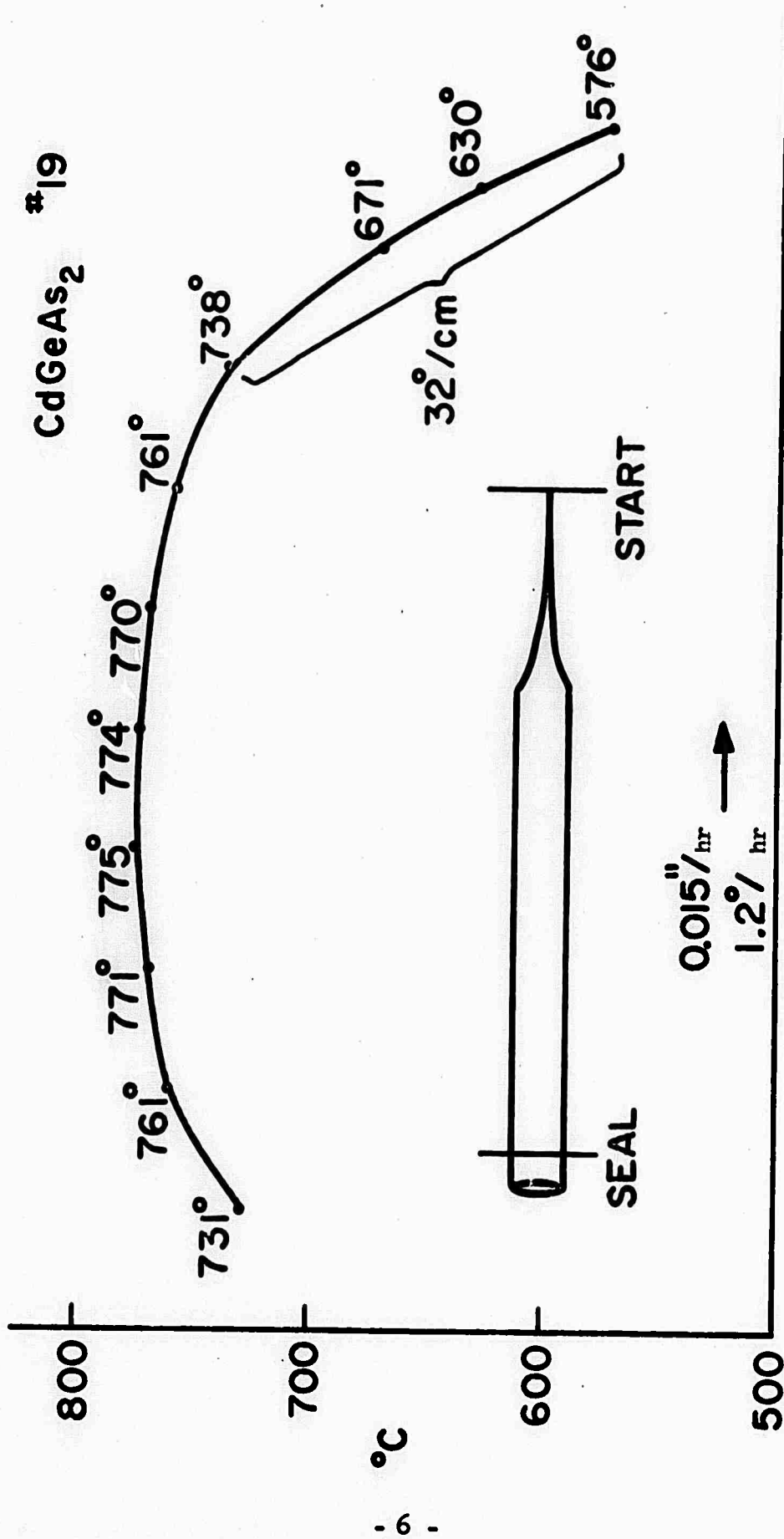


FIG. 2--Oven gradient and boule container for Bridgeman growth run #19.

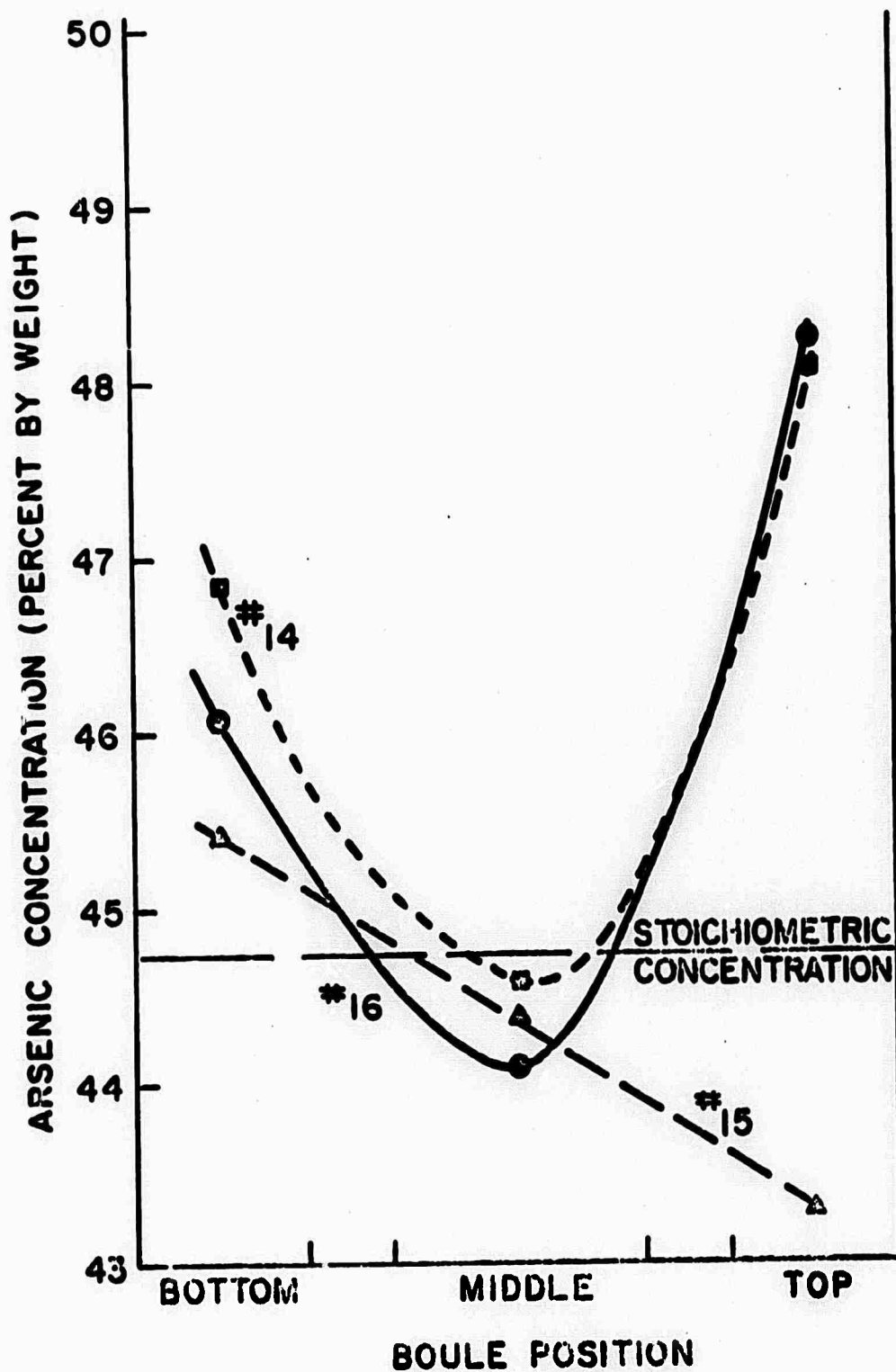


FIG. 3--Microchemical analysis of arsenic concentration in CdGeAs<sub>2</sub> samples.

first crystal runs through the zone refiner showed that the volume expansion of the  $\text{CdGeAs}_2$  was so severe as to cause the crucibles to crack.

The growth apparatus was modified to allow the use of a graphite crucible. Using this crucible with dimensions of 9 mm o.d., 7 mm i.d. by 4" long with a quartz envelope that enclosed the graphite loosely, a successful run through the zone furnace was made.

The resulting boule was 6 cm in length and very smooth and solid in appearance. It has been sectioned for optical and chemical analysis. The cracking was apparently reduced as first observed by the crack-free boule surface. Preliminary x-ray analysis showed that the boule was chalcopyrite structure with highly polycrystalline grains at one end and single crystal regions at the other. This result is very promising and is being pursued at the present time.

During the past quarter efforts have also been made to measure the  $\text{CdGeAs}_2$  index and birefringence. The problem has been attacked from two directions. First, efforts have been made to find a large enough single crystal to cut a small prism. This prism is to be used in a standard minimum deviation method to measure the crystal indices.

Secondly, efforts have been made to design and construct a very high precision index of refraction apparatus. The design to be used includes reflecting optics, thermocouple detector, high brightness thermal light source and atomic-line light sources. These components along with a grating spectrometer and 1/2 second arc accuracy angular table should allow index measurements to be made from the ultraviolet to the infrared region with an accuracy determined by the prism size, wavelength accuracy or both. In practice this limit is about one part in  $10^5$  which is accurate enough for a very good Sellmeier equation fit to the dispersion

curve. Computer programs to fit a five-constant fourth-order Sellmeier equation to the index of refraction data have already been developed at Stanford.

In conclusion, the progress made this quarter has been encouraging especially with respect to the transparency range and improved crystal quality of  $\text{CdGeAs}_2$ . These efforts are continuing to obtain material of such a size that accurate measurements of its properties can be made.